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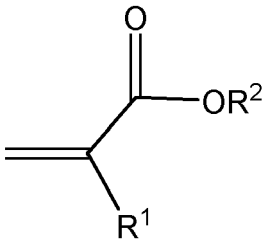
(71) Applicants:
- **Rohm and Haas Electronic Materials LLC**
  Marlborough, MA 01752 (US)
- **Rohm And Haas Electronic Materials Korea Ltd.**
  Chungcheongnam-do 331-980 (KR)
- **Dow Global Technologies Llc**
  Midland, MI 48674 (US)

(72) Inventors:
- **BAI, Zhifeng**
  Midland, MI Michigan 48674 (US)
- **JOO, Jaebum**
  Marlborough, MA Massachusetts 01752 (US)
- **SUNG, In-Kyung**
  331-980 Cheonan (KR)
- **TAYLOR, James C**
  Marlborough, MA Massachusetts 01752 (US)

(74) Representative: **Houghton, Mark Phillip**
Patent Outsourcing Limited
1 King Street
Bakewell, Derbyshire DE45 1DZ (GB)

(54) **MULTILAYER POLYMER COMPOSITE FOR ENCAPSULATING QUANTUM DOTS**

(57) A polymer composite comprising quantum dots and polymerized units of at least one compound of formula (I)



(I)

wherein R^1 is hydrogen or methyl and R^2 is a C_6-C_{20} aliphatic polycyclic substituent.

EP 3 070 109 A1

Description

FIELD OF THE INVENTION

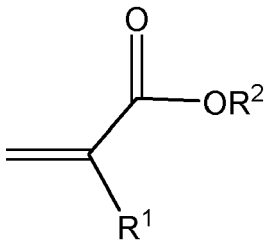
[0001] The present invention relates to a process for preparing a multilayer polymer composite containing quantum dots.

BACKGROUND OF THE INVENTION

[0002] Semiconductor quantum dots (QD) provide optical absorption and emission (photoluminescence PL or electroluminescence EL) behaviors that are significantly different from those of bulk materials. As the particle size decreases, effective energy bandgap (Eg), or available energy levels, increases and creates a blue shifted PL spectrum. This spectrum tunability by the particle size dependent quantum confinement effect within the same material is a critical advantage over conventional bulk semiconductors. Because of their unique optical properties, QD have been of great interest in many display and lighting applications. Most QD have inorganic shells with a larger bandgap material to confine electron and hole pairs within the core region and prevent any surface charge states. The outer shells are then capped by organic ligands to reduce trap states of the shell that can lead to reduced quantum yield (QY). Organic ligands help QD to disperse in organic/aqueous solvents. Typical organic ligands surrounding QD have relatively long alkyl chains which provide high solubility in non-polar solvents or monomers. Unfortunately, QD are very susceptible to photooxidation during light absorption/conversion process. Also, moisture can have similar impacts when ligands are not compatible. QD typically are encapsulated in a polymer matrix to protect them from adverse effects of water and oxygen. For example, US2010/0084629 discloses a variety of polymers as encapsulants. However, this reference does not disclose the polymer compositions described herein.

SUMMARY OF THE INVENTION

[0003] The present invention provides a polymer composite comprising quantum dots and polymerized units of a compound of formula (I)



(I)

wherein R^1 is hydrogen or methyl and R^2 is a C_6-C_{20} aliphatic polycyclic substituent.

DETAILED DESCRIPTION OF THE INVENTION

[0004] Percentages are weight percentages (wt%) and temperatures are in °C, unless specified otherwise. Operations were performed at room temperature (20-25 °C), unless specified otherwise. Boiling points are measured at atmospheric pressure (ca. 101 kPa). The term "(meth)acrylate" means acrylate or methacrylate. Quantum dots are well known in the art, see, e.g., US2012/0113672.

[0005] In one preferred embodiment of the invention, the polymer composite is part of a multilayer assembly which also comprises an outer layer on each side of the polymer composite. Preferably, the outer layer is an oxygen barrier which also inhibits passage of moisture. Preferably, the outer layer comprises a polymer film, preferably one comprising polyethylene terephthalate (PET), polyaryletherketones, polyimides, polyolefins, polycarbonate, polymethyl methacrylate (PMMA), polystyrene, or a combination thereof. Preferably, the outer layer further comprises oxides or nitrides, preferably silicon oxides, titanium dioxide, aluminum oxide, silicon nitrides or a combination thereof. Preferably the oxides or nitrides are coated on the surface of the polymer film facing the QD layer. Preferably, each outer layer comprises a polymer film having a thickness from 25 to 150 microns (preferably 50 to 100 microns) and an oxide/nitride layer having a thickness from 10 to 100 nm (preferably 30 to 70 nm). In some preferred embodiments of the invention, the outer layer comprises at least two polymer film layers and/or at least two oxide/nitride layers; different layers may be of differing composition. Preferably, the outer layers have a very low oxygen transmission rate (OTR, < 10^{-1} cc/m^2/day) and low water vapor transmission rate (WVTR, < 10^{-2} g/m^2/day). Preferably, the polymer film in the outer layers has a Tg from 60 to 200°C;

preferably at least 90°C, preferably at least 100°C.

[0006] Preferably, the thickness of the polymer composite ofthis invention is from 10 to 500 microns, preferably at least 20 microns, preferably at least 30 microns, preferably at least 40 microns; preferably no greater than 400 microns, preferably no greater than 300 microns, preferably no greater than 200 microns, preferably no greater than 150 microns. Preferably, the thickness of each outer layer is from 20 to 100 microns, preferably from 25 to 75 microns

[0007] Preferably, the polymer composite of this invention is prepared by free radical polymerization of the resin prepared by mixing monomers, QD and other optional additives. Preferably, the resin is coated on a first outer layer prior to curing by typical methods, e.g., spin coating, slot die coating, gravure, ink jet and spray coating. Preferably, curing is initiated by exposing the resin to ultraviolet light or heat, preferably ultraviolet light, preferably in the UVA range.

[0008] Preferably, R^2 is a C_7-C_{17} aliphatic polycyclic substituent, preferably R^2 is a C_8-C_{15} aliphatic polycyclic substituent. Preferably, R^2 is a bridged polycyclic substituent; preferably a bicyclic, tricyclic or tetracyclic substituent; preferably a bicyclic or tricyclic substituent. Preferably, R^2 is a saturated aliphatic substituent. Preferred structures for R^2 include, e.g., adamantanes, bicyclo[2,2,1]alkanes, bicyclo[2,2,2]alkanes, bicyclo[2,1,1]alkanes and tricyclodecanes (e.g., tricyclo[52,1,$0^{2,6}$]decane), these structures may be substituted with alkyl, alkoxy groups, hydroxy groups or (meth)acrylate esters (i.e., the compound of formula (I) may have at least two (meth)acrylate ester substituents; preferably no more than two); preferably alkyl and alkoxy groups have from one to six carbon atoms, preferably one to four. Tricyclodecanes and bicyclo[2,2,1]alkanes are especially preferred, particularly 1ricyclo[5,2,1,$0^{2,6}$]decane, dimethanol dimethacrylate and isobornyl acrylate. Preferably, the inner layer comprises polymerized units of a compound of formula (I) having one (meth)acrylate ester substituent and a compound of formula (I) having two (meth)acrylate ester substituents; preferably in a weight ratio from 100:1 to 1:5, respectively; preferably 10:1 to 1:2

[0009] Preferably, the polymer composite ofthis invention comprises from 0.01 to 5 wt% of quantum dots, preferably at least 0.03 wt%, preferably at least 0.05 wt%; preferably no more than 4 wt%, preferably no more than 3 wt%, preferably no more than 2 wt%. Preferably, quantum dots comprise CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, GaN, GaP, GaAs, InP, InAs or a combination thereof

[0010] Preferably, ligands surrounding the inorganic part of quantum dots have non-polar components. Preferred ligands include, for example, .trioctyl phosphine oxide, dodecanethiol and fatty acid salts (e.g., stearate salts, oleic acid salts).

[0011] Other additives which may be incorporated into the polymer composite ofthis invention include uv stabilizers, antioxidants, scattering agents to improve light extraction, and thickeners to increase viscosity (e.g., urethane acrylate oligomers). Preferred thickeners include urethane acrylates, cellulose ethers, cellulose acrylic esters, polystyrene polymers, polystyrene block copolymers, acrylic resin and polyolefin elastomers.. Preferably, polystyrene, acrylic and polyolefin thickeners have Mw from 50,000 to 400,000; preferably from 100,000 to 200,000. Preferably, cellulose ethers have Mw from 1,000 to 100,000.

[0012] Urethane acrylate oligomers can be polyester type, polyether type, polybutadiene type, or polycarprolactone type. They can have difunctional, trifuctional, hexafunctional reactivities. Viscosities of oligomers can range from 1000 to 200,000 cPs at 50C. For non-polar ligand QDs, polybutadiene types are preferred.

[0013] Preferably, the first inner layer comprises from 1 to 60 wt% urethane acrylates, preferably at least 5 wt%, preferably at least 10 wt%; preferably no more than 50 wt%, preferably no more than 40 wt%.

[0014] Preferred forms for the polymer composite include, e.g., films, beads, strips, rods, cubes and plates. The polymer composite is useful in many applications, including, e.g., displays, lighting and medical applications. Preferred display applications include public information displays, signage, televisions, monitors, mobile phones, tablets, laptops, automotive dashboards and watches.

EXAMPLES

SAMPLE PREPARATION FOR EXAMPLES

[0015] All samples were prepared by lamination of the resin formulations between two i-Component PET barrier films. Approximately 2mL of resin was dispensed on the bottom film and the top has applied with a gap coating bar with gap setup (10mil - 12mil) based on desired film thickness. Samples were cured in a Fusion UV F300S curing system with UVA 400mJ/cm^2, unless otherwise noted. Film thicknesses were determined by measurement of the cured films with a micrometer and then subtracting out the barrier film thickness. Photoluminescent Quantum Yield (PLQY), peak emission wavelength (PWL) and full-width half-max of the emission peak (FWHM) were measured with a Hamamatsu C9920-02G integrating sphere. Edge ingress was determined by image analysis of 1"x1" samples aged on a bare backlight unit.

EXAMPLE 1: Comparison of linear aliphatic monomers to cycloaliphatic monomers

[0016]

Curing condition: UVA 400mJ/cm^2 x 4times

	Formulation A	Formulation B	Formulation C	Formulation D
Nanoco CFQD[1] quantum dot	0.7	0.7	0.7	0.7
Lauryl acrylate	35.8	0	0	0
Isobornyl acrylate	0	35.8	32.7	29.6
Tricyclodecane dimethanol diacrylate	0	0	5	10
IRGACUREI-819	2.5	2.5	2.5	2.5
Trimethylolpropane tris(3-mercaptopropionate	4	4	4	4
Trimethylolpropane triacrylate	14	14	14	14
CN996 oligomer	42	42	40.1	38.2
$BaSO_4$	1	1	1	1

1. Cadmium-free quantum dots as described in US7588828

[0017] CN996 oligomer is an aliphatic urethane acrylate oligomer, from Sartomer America.]

Coating thickness:

FilmID	QD display film thickiness mm
Formulation A	0.117
Formulation B	0.110
Formulation C	0.135
Formulation D	0.121

Edge ingress damage after 1000Cd/m^2 blue BLU

	24Hr	96hours	120hr	168hr	336hr
Formulation A	0.764417	1.276159		1.727667	2.248431
Formulation B	0	0.336642		0.414909	0.46959
Formulation C	0		0.333269	0.382147	0.435117
Formulation D	0		0.26699	0.294882	0.427014

EXAMPLE 2: Examples of resin with antioxidant (IRGAFOS 168) and light stabilizer (TINUVIN 5100)

[0018]

	1	2	3
Nanoco CFQD quantum dot	0.14	0.14	0.14
Isobornyl acrylate	46.61	46.11	45.11
Tricyclodecane dimethanol diacrylate	30	30	30
IRGACUREI-819	1.5	1.5	1.5
IRGAFOS 168	0	0.5	0
TINUVIN 5100	0	0	1.5
BR-641D oligomer	17	17	17

(continued)

	1	2	3
TIPURE 706 TiO_2 particle	7.5	7.5	7.5

[0019] BR-641D oligomer is a polybutadiene urethane acrylate oligomer, from Dymax.]

[0020] TIPURE 706 is available from Dupont.

[0021] Curing: 400mJ/cm^2. Single pass

ID	avg (μm)
1	60
2	72
3	58

	PLQY	QY stdev	PWL	FWHM
1	37.77	1.86	517.95	57.76
2	42.77	1.17	518.20	56.55
3	42.53	0.65	519.68	55.07

EXAMPLE 3:

Example of resin prepared with polymer viscosity modifier (KRATON G1650)

[0022]

	Formulation A	Formulation B
Nanoco CFQD™ quantum dot	0.2	0.2
Isobornyl acrylate	68.5	58.7
Tricyclodecane dimethanol diacrylate	20	30
IRGACUREI-819	1.5	1.5
KRATON G1650	7.8	7.6
Zoco 101 ZnO particle	2	2
Zoco101 is available from Zochem.		

ID	avg (μm)
Formulation A	39
Formulation B	22

	PLQY	PWL	FWHM
Formulation A	41.4	638.9	59.6
Formulation B	40.5	648.3	61.4

EXAMPLE 4:

[0023] Examples of resin prepared with various ratios of cycloaliphatic monomers

	1	2	3	4
Nanoco CFQD quantum dot	0.05	0.05	0.05	0.05
Isobornyl acrylate	60.7	50.7	40.7	30.7
Tricyclodecane dimethanol diacrylate	20	30	40	50
IRGACUREI-819	1.5	1.5	1.5	1.5
BR-641D Oligomer	17	17	17	17
TIPURE 706 TiO_2 particle	0.75	0.75	0.75	0.75

ID	avg (μm)
1	132
2	133
3	107
4	123

Sample ID	AVG QY	STDEV QY	AVG PL	AVG FWHM	AVG PL RED	AVG FWHM RED
1	60.40	1.14	519.03	56.72	634.19	63.19
2	51.43	0.31	519.70	55.45	643.86	63.90
3	47.33	0.87	515.20	61.46	640.14	61.53
4	45.13	0.25	529.94	70.81	642.13	64.27

[0024] Edge Ingress damage (mm) after storage in 60°C/90% Relative Humidity

	72hr	168hr	336hr
1	1.72	3.17	5.77
2	1.49	2.33	3.78
3	0.86	1.50	2.41
4	0.64	1.10	1.78

EXAMPLE 5:

[0025] Examples of resin prepared with small loadings of linear aliphatic monomers as compatibilizing additives

	7	9
Nanoco CFQD™ quantum dot	0.04	0.04
Isobornyl acrylate	53.71	49.73
Lauryl methacrylate	0	3.96
Tricyclodecane dimethanol diacrylate	19	19
IRGACUREI-819	1.5	1.5

(continued)

	7	9
BR-641D Oligomer	25	25
TIPURE 706 TiO2 particle	0.75	0.75

ID	avg (μm)
7	53
9	45

	PLQY	QY stdev	PWL	FWHM
7	32.9	0.44	637.7	66.6
9	36.9	0.55	637.4	64.1

EXAMPLE 6: Examples of resin prepared with two different quantum dot mixtures.

[0026]

	1
Nanoco CFQD™ green quantum dot	0.28
Nanoco CFQD™ red quantum dot	0.07
Isobornyl acrylate	40.525
Tricyclodecane dimethanol diacrylate	30
IRGACUREI-819	15
KRATON G1652	9.125
TINUVIN 123	1.5
Zoco 101 ZnO particle	3.5

ID	avg (μm)
1	104

[0027] The cured film was placed between the light guide plate and prism film/brightness enhancement film of blue LED based backlight unit (BLU). BLU spectrum was measured using GL Spectis spectroradiometer. Color coordinate of final spectrum and color gamut coverage were calculated based on the BLU spectrum and an available color filter dataset.

	CIEx	CIEy	CIEz
BLU white	0.251	0.239	0.510
Panel blue	0.157	0.057	0.786
Panel green	0.246	0.694	0.060
Panel red	0.677	0.312	0.011
Panel white	0.262	0.276	0.461

	Color gamut coverage (vs. sRGB)
% area	138
% overlap	100

[0028] Wavelength dependent emission spectrum normalized by the maximum peak intensity.

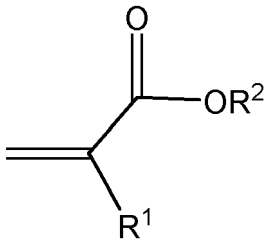
wavelength	blue LED BLU	blue LED BLU + film
400	0.001799541	-0.001718333
405	0.005268541	0.000577671
410	0.016890786	0.007631886
415	0.04931601	0.028007319
420	0.122586966	0.081087041
425	0.265607892	0.199143175
430	0.511079238	0.430434011
435	0.833891183	0.774125936
440	1	0.991670706
445	0.864842533	0.898225587
450	0.57331293	0.61091274
455	0.339906003	0.363499942
460	0.199517423	0.211355149
465	0.11107564	0.117340634
470	0.063158431	0.069497716
475	0.037262744	0.047296871
480	0.021987463	0.037964307
485	0.012910007	0.038338101
490	0.007966666	0.046298448
495	0.005238596	0.061020953
500	0.003220408	0.084885063
505	0.002313958	0.120505083
510	0.001915676	0.168584908
515	0.001401463	0.225699285
520	0.000859068	0.285145182
525	0.000923902	0.335413153
530	0.00049007	0.362652675
535	0.00069194	0.36050481
540	0.00045016	0.335668494
545	0.000403799	0.293595319
550	7.34827E-05	0.244397867
555	0.000133896	0.194297165
560	3.49273E-05	0.151623188

(continued)

wavelength	blue LED BLU	blue LED BLU + film
565	-1.87684E-05	0.11996641
570	-4.49488E-05	0.096343986
575	7.58107E-05	0.078691345
580	7.31695E-05	0.06614026
585	-0.000314182	0.057090482
590	-0.000335826	0.052079524
595	7.39134E-05	0.051888975
600	-0.000278013	0.05624342
605	-0.000346791	0.066283223
610	-0.000459618	0.083073783
615	-0.000457154	0.106960422
620	-0.000748242	0.13759379
625	-0.000716673	0.175583563
630	-0.000522994	0.215143612
635	-0.000838996	0.249540865
640	-0.000543793	0.274591557
645	-0.000512196	0.286686784
650	-0.000598369	0.287997624
655	-0.000886423	0.279322187
660	-0.000449722	0.261573281
665	-0.000750665	0.238296318
670	-0.00101099	0.210964628
675	-0.001141071	0.183288842
680	-0.001147285	0.157807348
685	-0.001269858	0.136076083
690	-0.001727023	0.116518628
695	-0.00166393	0.098685064
700	-0.001698529	0.0847294
705	-0.001551849	0.070714339
710	-0.00270767	0.057980488
715	-0.003036792	0.046570789
720	-0.004571635	0.036315994
725	-0.009056433	0.02743212
730	-0.009250231	0.017445023
735	-0.0078037	0.010043558
740	-0.007486296	0.00546386
745	-0.007656289	0.004965795
750	-0.00738996	0.00555811

Claims

1. A polymer composite comprising quantum dots and polymerized units of at least one compound of formula (I)



(I)

wherein R^1 is hydrogen or methyl and R^2 is a C_6-C_{20} aliphatic polycyclic substituent.

2. The polymer composite of claim 1 in which R^2 is a bridged polycyclic substituent.

3. The polymer composite of claim 2 in which R^2 is a C_7-C_{17} bridged polycyclic substituent.

4. The polymer composite of claim 3 in which the polymer composite comprises a compound of formula (I) having one (meth)acrylate ester substituent and a compound of formula (I) having two (meth)acrylate ester substituents in a weight ratio from 100:1 to 1:5, respectively.

5. The polymer composite of claim 4 in which R^2 has a bicyclo[2,2,1]alkane or tricyclodecane ring system.

6. The polymer composite of claim 5 in which the quantum dots comprise CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, GaN, GaP, GaAs, InP, InAs or a combination thereof.

7. The polymer composite of claim 6 further comprising a urethane acrylate, a cellulose ether, a cellulose acrylic ester, a polystyrene polymer, a polystyrene block copolymer, an acrylic resin or a polyolefin elastomer.

8. The polymer composite of claim 6 further comprising a scattering agent.

9. The polymer composite of claim 8 further comprising an antioxidant or UV light stabilizer.

10. The polymer composite of claim 6 which is a film.

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EUROPEAN SEARCH REPORT

Application Number
EP 16 15 2914

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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A	US 2014/264193 A1 (DANIELS SIOBHAN [GB] ET AL) 18 September 2014 (2014-09-18) * paragraphs [0003], [0015], [0016]; claims 1-10; example 1 *	1-10	

TECHNICAL FIELDS SEARCHED (IPC)

C08F
B32B
C09D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	28 April 2016	Giani, Elena

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 16 15 2914

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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